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Abstract

In order to understand the physico-chemical mechanisms governing interactions between hemp fibres and a lime-based mineral matrix, the consequences of various chemical treatments onto hemp fibres characteristics were measured using scanning electron microscopy, thermal analysis, X-ray diffraction and FTIR spectroscopy. Secondly, effects of these treatments on the mechanical properties of lime mortars incorporating the chemically modified fibres were evaluated using 3 point bending tests.
NaOH and EDTA treatments increase the crystallinity index of hemp fibres and increase the experimental rigidity of lime/natural fibres mortars. Treatments with polyethylene imine and a saturated lime solution do not induce any significant changes onto the mechanical properties.
These results show that some specific chemical treatments have an impact onto the hemp/lime interfaces quality. The elaborated composite materials exhibit a higher rigidity and an improvement of the matrix /fibre charge transfer. However, the rupture stress is only slightly modified due to a relatively low fibre volumic content (10 %).

Keywords

natural fibre, composites, surface treatment, mechanical properties

Introduction

Lime-based mortars have been used for centuries as stone binders in ancient buildings. During the 20th century, the use of lime in construction disappeared due to the fast development of Portland cement [1]. Nevertheless, over the past several decades, the need to develop environmentally-friendly products has generated new interest in using lime as a building material.
Many studies on lime-based mortar were carried out in order to understand the influence of various parameters, like viscosity, pore structure, capillary porosity and water/lime ratio, in particular on the mechanical properties of resulting mortars [2-5]. To date, no investigation of the incorporation of natural fibres in a lime matrix were reported, although natural fibres were introduced in polymers or cement matrices and are known to improve mechanical properties of mortars [6-8].
The use of natural fibres and in particular hemp fibres as reinforcing agents in composite materials offers many advantages over glass fibres, such as low density and biodegradability [6-9-10]. However, their incorporation in a polymer or mineral matrix involves an interface incompatibility between fibres and matrix which may be overcome with fibres chemical pre-treatments [11-13]. Each treatment considered in this publication modifies either the chemical nature of the surface of natural fibres, or the surface state (e.g.: charge, conformation of polymers). The consequence is probably a modification of the interactions between the mineral matrix and fibres. For example, treatment with sodium hydroxide removes amorphous materials, such as hemicelluloses, lignins and pectins, from the hemp fibres surface, and this in turn would probably increase the crystallinity index of fibres [13-15].
The adsorption in large quantity of calcium ions on fibres surface can influence the fibre/matrix interface [16]. To check the impact of the calcium adsorption, two approaches were selected. In a first treatment, fibres were treated with acid ethylene-diamine-tetracetic (EDTA) which forms with calcium ions a very stable complex and disturb the complex formed between pectins and calcium ions [17]. This treatment would prevent the fixing of calcium ions on the surface of fibres. The second treatment consists in modifying the negative charge surface of fibres using a cationic polyelectrolyte, polyethylene imine (PEI), in order to prevent the fixation of calcium ions [18]. Lastly a lime water solution was used to test the influence of pH in calcium ions adsorption [19].

Experimental

Fibre surface treatments

Prior to treatment and in order to ensure a constant humidity content, fibres were dried at 40°C for 24 h in a drying oven.
In order to improve the adhesion between fibres and the mineral matrix, fibres were subjected to several surface treatments:

- Alkalization: Dried fibres were soaked in 0.06 M. NaOH solution during 48 h and then neutralized with 1 % vol. acetic acid. Fibres were then washed with deionised water until the pH value was 7.
- EDTA: Fibres were immerged during 3 h in a solution of EDTA (5g/l) which pH was adjusted to 11 with caustic soda. In order to ensure removal of excess EDTA, fibres were then washed with deionised water for two hours.
- PEI: Fibres were soaked in a PEI (M.W: 2000 g.mol^{-1}) solution for 48 h, then washed with deionised water.
- $Ca(OH)_2$: In order to saturate fibres with calcium ions, fibres were placed for 3 hours in a saturated lime solution ($[Ca^{2+}]$ =2.10^{-2} M, pH=12.7). Following the impregnation, fibres were washed with deionised water.

After all treatments, fibres were subsequently dried at 40 °C for 24 h.

Characterisation

A Scanning electron Microscope (SEM) (Cambridge stereoscan S260) was used to examine the effects of chemical modifications upon the fibre surface. Samples are obtained by cutting small pieces of fibres and sticking them on a carbon adhesive, before coverage with a platinum film.

Differential scanning calorimetry (DSC) measurements were performed under dry atmosphere using a Setsys 2400 instrument (SETARAM). Temperature ranged from 25°C to 800°C with a heating rate of 5°C.min^{-1}.

In order to assess the influence of the treatments on fibre crystallinity, XRD experiments were carried out using a home-made diffractometer deriving from the Debye-Scherrer geometry and based [20] on a sealed tube operating at 37.5 kV / 28 mA, a curved quartz monochromator (Cu $K_{\alpha 1}$ radiation) and a curved position sensitive detector (Inel CPS 120).

Fibres were cut with a knife crusher to about 500µm and pressed into a pellet using a cylindrical steel mould (ϕ = 16 mm) with an applied pressure of 35 MPa in a laboratory press.

The crystallinity index (CI), which is a measurement of the amount of crystalline cellulose with respect to the global amount of amorphous materials, was evaluated using an internal standard method [21]. It is well-known that the intensity of a diffraction peak corresponding to a phase is directly proportional to the volumic quantity of phase presents in the homogeneous mixture. In order to evaluate the proportionality coefficient, a standard $Ca(OH)_2$ was mixed in various proportions with microcrystalline cellulose (Avicel), for which the amount of crystalline cellulose is known.

Crystallinity indexes were determined while comparing the diffraction peak intensity of $Ca(OH)_2$ and crystalline cellulose in the preceding mixture and in a second one wich contained hemp fibres and 30% wt. $Ca(OH)_2$.

FTIR measurements were performed using a Perkin Elmer spectrometer (Spectrum one, Boston, U.S.A.) using the standard KBr pellet technique. A total of 10 scans was taken for each sample between 400 cm^{-1} to 4000 cm^{-1}, with a resolution of 4 cm^{-1}. Fibres were chopped roughly to a length of less than 1 mm and mixed with 300 mg of KBr and then pressed into a pellet (ϕ= 16 mm) for FTIR measurement.

The flexural strength of the composite before and after chemical treatments were determined using a three-point bending test method (EZ 20 Lloyd Instrument, AMETEK). The crosshead speed applied was 0.1 mm/min. Each sample was loaded until the core broke and the average over 10 measurements is reported.

Results and Discussion

Impact of chemical treatments on fibres

Surface morphology

Scanning electron microscopy provides an excellent technique for examination of surface morphology of natural and treated fibres [17].

Micrographs of untreated fibres, such as the one presented in Fig1-a indicates the presence of impurities on surface, mostly waxes and oil. However, after alkali or PEI treatment, as presented in Fig1-b and Fig1-d, a surface free of impurities is obtained. Observation of micrographs obtained after the EDTA treatment (Fig1-c) seemed to separate fibres. Indeed, it was previously reported that EDTA, a calcium chelatant, captures calcium present in pectins aggregates to form a stable complex, this in turn induces the separation of fibres. On the contrary, a lime treatment tends to saturate the surface with calcium nodules, as reported by Sedan et al (Fig1-e) [19].

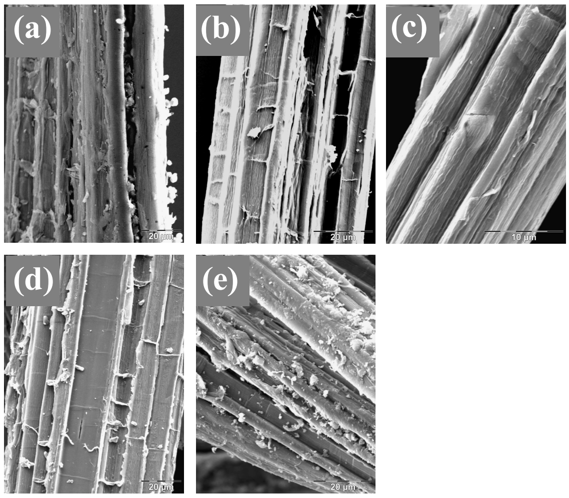

Figure 1: SEM images of (a) untreated, (b) NaOH, (c) EDTA, (d) PEI and (e) $Ca(OH)_2$ treated hemp fibres

Thermal analysis of fibres

Thermal analysis can be performed to determine the moisture content and the amount of volatile components present in fibres.

Independently of chemical treatments, differential thermal analysis curves show a first endothermic peak between temperature of 50 and 175 °C, which is caused by the evaporation of weakly bound water molecules.

The DSC curve of untreated natural fibres, presented in Figure 2, presents three exothermic reactions: a first peak located between 250 and 320°C is attributed to the thermal depolymerisation of hemicelluloses and pectins. A signal between 390 and 420°C is attributed to the cellulose decomposition. Finally, a last peak at higher temperatures represents decomposition of lignin residues [22].

The first peak is shifted at higher temperatures with caustic soda (≈335°C) and lime saturated solution treatment (≈355°C), which signifies that after treatments in a strongly basic medium, modified hemp fibres are thermally more stable than untreated ones.

The peak characteristics of cellulose decomposition is shifted at higher temperatures with caustic soda (≈410°C) and PEI (≈450°C) treatments, whereas EDTA and a saturated lime solution treatments decrease the initial temperature of decomposition of cellulose by 10 and 20°C respectively. PEI and caustic soda make the cellulose more stable towards heat decomposition. In particular, PEI treatment seems to act as a protection on the surface of fibres and prevents the decomposition of cellulose [22].

This result seems to indicate that NaOH treatment preferentially degrades amorphous polysaccharides, leaving crystalline and heat-resistant cellulose molecules behind.

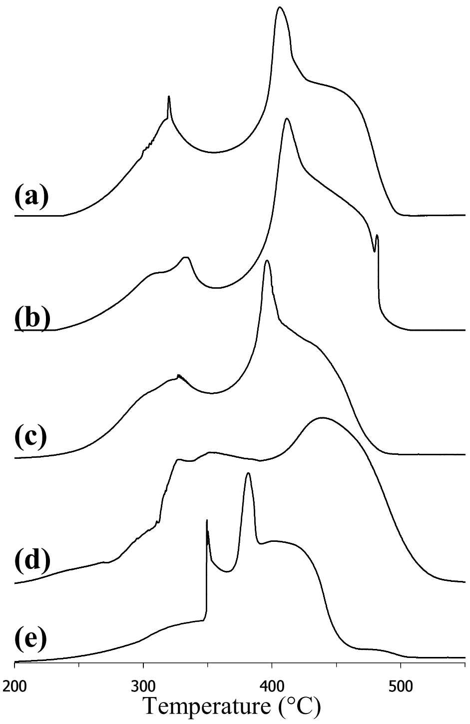

Figure 2: Comparison of the DSC curves as a function of the chemical treatment of the hemp fibres (a) untreated, (b) NaOH, (c) EDTA, (d) PEI and (e) $Ca(OH)_2$

X-ray diffraction

Cellulose exists under several polymorphic states, the most well-known and studied one being cellulose I, or native cellulose, which is the crystalline form detectable by X-ray diffraction. The other states are amorphous (cellulose II, III, IV). Figure 3 shows the diffractogram obtained for untreated, NaOH and $Ca(OH)_2$ treated fibres.

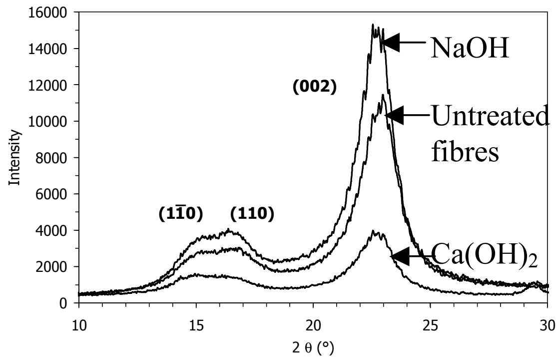

Figure 3: X-ray patterns of untreated and treated hemp fibres.

It presents a major crystalline peak for 2θ ranging between 22 and 23°, which corresponds to the (002) crystallographic plane family of cellulose I.

The two other peaks present at 2θ =15.2° and 2θ =16.8° correspond respectively to the $(1\bar{1}0)$ and (110) crystallographic planes. For a high percentage of crystalline cellulose I, these two peaks are quite marked and distinct, whereas when the fibres contain a strong percentage of amorphous material (i.e. lignin, pectins, hemicelluloses and amorphous cellulose), these two peaks are superimposed .

Table 1 presents the crystallinity index obtained using an internal standard method.

Chemical treatment	Untreated fibres	NaOH	EDTA	PEI	$Ca(OH)_2$
Crystallinity index	59	77	71	73	57

Table 1: Crystallinity index

These data show that treatments with EDTA, PEI and NaOH increase the value of the crystallinity index.

Indeed, EDTA treatment forms a very stable complex with calcium ions, which removes pectin/calcium complex present on the fibre surface.

The PEI amin groups react with cellulose carbonyl groups following reaction (1) [23].

$$\text{(Cellulose)-C=O} + \text{(PEI)-NH}_3^+ \leftrightarrow \text{(Cellulose)-C=N-(PEI)} + H_2O \quad (1)$$

This reaction is probably at the origin of the crystallinity index increase.

Alkali treatment hydrolyzes the amorphous parts of cellulose present in fibres and after treatment the material contains more crystalline cellulose. The reaction between cellulose and caustic soda is described by reaction (2):

$$\text{Cellulose-OH} + NaOH \rightarrow \text{Cellulose-O}^- Na^+ + H_2O + \text{impurities} \quad (2)$$

Na^+ ions come to fit in the unit cell of cellulose, increasing the cell parameter [24].

However, $Ca(OH)_2$ treatment has little impact on the crystallinity index.

Fourier Transform Infrared Spectroscopy

FTIR allows the measurement of variations of hemp fibre composition after chemical treatments. Table 2 summarizes the major bands observed in the FTIR spectrum of hemp fibres and their assignments to chemical group vibrations and molecules.

Wavenumber (cm^{-1})	Vibration	Source
3300	O-H linked shearing	Polysaccharides
2885	C-H symetrical stretching	Polysaccharides
2850	CH2 symetrical stretching	Wax
1732	C=O unconjugated	Xylans (Hemicelluloses)
1650-1630	OH (water)	Water
1505	C=C aromatic symetrical stretching	Lignin
1425	CH2 symetrical bending C=C stretching in aromatic groups	Pectins, lignins, hemicelluloses, calcium pectates
1370	in-the-plane CH bending	Polysaccharides
1335	C-O aromatic ring	Cellulose
1240	C-O aryl group	Lignin
1162	C-O-C asymetrical stretching	Cellulose, hemicellulose
895	glycosidic bonds	Polysaccharides
670	C-OH out-of-plane bending	Cellulose

Table 2: Infrared principal bands

Infrared spectra of hemp fibres without and with chemical treatment are displayed in fig 4.
Modifications in the FTIR spectra are principally observed in the 400-4000 cm^{-1} range. One of the most noticeable modification generated by all chemical treatments is the disappearance of the peak centered at 1732 cm^{-1}, characteristic of hemicelluloses. Indeed, treatments with lime water, PEI and NaOH, are known to remove hemicelluloses [25].The observation of the peak located at 1505 cm^{-1} after all treatments seems to indicate that none of the chemical treatment is successful in completely removing lignin from hemp fibres. With caustic soda treatment, the intensity of the peak characteristic of waxes and oils present at 2850 cm^{-1} decreases whereas the intensity of the peak characteristic of polysaccharides hydroxyl bonds and located near 3300 cm^{-1} increases (Table 2).

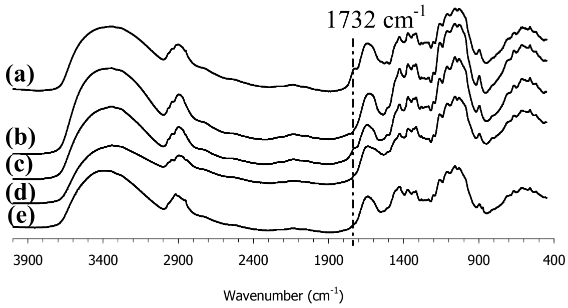

Figure 4: FTIR spectra (4000-2000 cm^{-1}) of (a) untreated, (b) NaOH, (c) EDTA,(d) PEI and (e) $Ca(OH)_2$ treated hemp fibres

The intensity of the peak at 1650-1630 cm^{-1}, which corresponds to water absorbed in cellulose, increases slightly after treatment with caustic soda. Indeed, NaOH react with –OH present on cellulose to form water molecules.
Some authors differentiate the peaks associated to pectins [25]:
- esterified pectins have three characteristic peaks at 1748, 1445 and 1234 cm^{-1}. These three weak peaks are difficult to dissociate from the signals relative to others
- calcium pectates result in the presence of a signal at 1615 cm^{-1} and a broad band in 1425 cm^{-1}. The first peak is very difficult to dissociate from the water signal. As for the peak at 1425 cm^{-1}, it is also characteristic of the CH bonds present in all organic molecules. In order to analyze the percentage of calcium pectates, it would be necessary to first completely remove the water molecules from hemp fibres.

Influence of the chemical treatment on mechanical properties of mortars

Prior to mortars preparation, fibres were cut to a length of approximately 1 cm and then further separated with a laboratory blender (Warring laboratory, Torrington, USA). The final length distribution of fibres ranged between 1 mm and 1 cm. The mixture is carried out by adding fibres to lime in a mixer (Labotest Perrier, type 32, France) during 2 min, followed by water addition. In all cases, the water/lime ratio (E/C) was kept at a constant value of 0,62.
Figure 5 represents the evolution of the force applied according to the arrow on the centre of a pure lime prism and for a sample with 10% vol. of fibres.

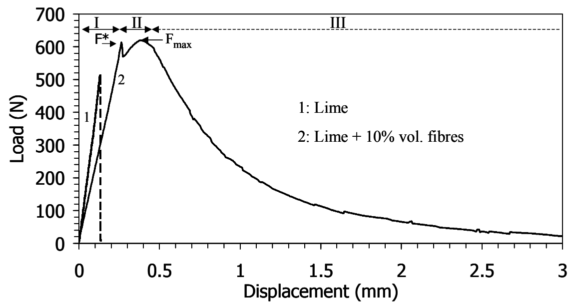

Figure 5: Three point bending test

Introduction of hemp fibres into a mineral matrix, such as lime, modifies the linear and fragile character of the matrix (1) to give a typical composite behaviour (2), for which 3 principal domains and 2 characteristic points are observed. The point F *, from which a decrease of load is observed, corresponds to the point of first macroscopic damage of the composite. The F_{max} point corresponds to the maximum force applied. In domain I [O-F *], the material exhibits a linear behaviour. This domain, where the load is supported only by the matrix, is representative of the lime behaviour. In domain II [F*-F_{max}], the behaviour of material is non-linear with a load transfer towards the fibres. At the point associated with F *, a hook of total decoherence of fibre in the matrix is observed, which represents the extraction and the friction of fibre in the sheath of the matrix, followed

Type of fibres contained in the lime mortar	Maximum stress ± scattering (MPa)	Displacement (mm)	Experimental rigidity (kN/mm)		Rt-Rs / Rt (%)
			Before F*: Rt	After F*: Rs	
No fibres	1.54 ±0.14	0.16	3.86	3.86	0.00
Untreated fibres	1.89 ± 0.23	0.65	1.09	0.92	0.16
NaOH treated fibres	1.92 ± 0.16	0.29	2.59	2.05	0.21
EDTA treated fibres	2.01 ± 0.05	0.4	1.67	1.61	0.04
PEI treated fibres	1.95 ± 0.22	0.48	1.51	1.30	0.14
$Ca(OH)_2$ treated fibres	1.43 ± 0.21	0.42	1.32	1.25	0.05

Table 3: Influence of chemical treatments on the results obtained in three-point bending test.

by an increase in effort. This load transfer from the lime matrix to the hemp fibres allows a slight increase in the maximum stress average and a reduction in the total rigidity of the composite (Table 3): this can be regarded as the beginning of the macroscopic damage. At the point associated with F_{max}, the rupture of composite material occurs and is accompanied by a progressive decrease of the applied force.

Experimental rigidities presented in table 3 were obtained by calculating the slope from the origin (Rt) and the slope between the origin and Fmax (Rs), as depicted in figure 6.

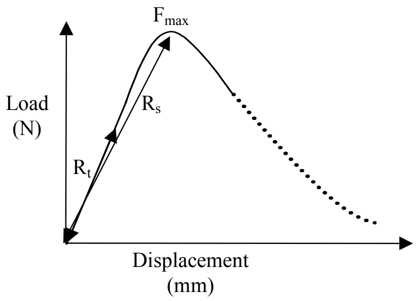

Figure 6: Experimental rigidity

Contrary to what is observed for a pure lime sample, the composite presents a controlled load decrease associated with a progressive rupture of the interfaces between the matrix and hemp fibres, followed by a washing away and a rupture of fibres. Introduction of hemp fibres increases by 23% the stress average compared to lime samples prepared without fibres (Table 3). Fibres treated with EDTA and $Ca(OH)_2$ cause extreme variations of stress average. EDTA increases the stress average of 6%, whereas with a lime solution, we observe a decrease in stress average of 24 %.

The decrease of rigidity reveals the progression of a macroscopic damage in the sample. Figure 7 shows the impact of crystallinity on rigidity of mortars. Fibres crystallinity has a direct impact on rigidity of resulting mortars. NaOH treated fibres have the strongest index of crystallinity as well as the strongest rigidity, whereas untreated and $Ca(OH)_2$ treated fibres have the lowest cristallinity and rigidity.

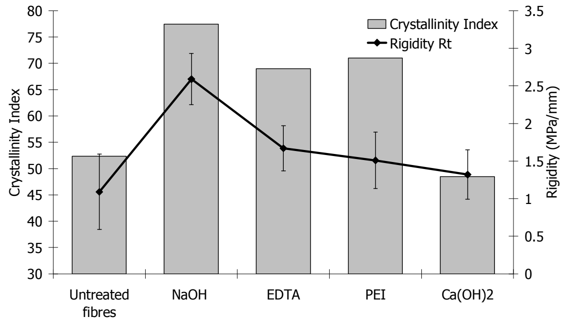

Figure 7: Impact of crystallinity on rigidity

Conclusion

The objective of this work was to explore the potentialities of reinforcement of a lime mineral matrix with hemp fibres by improving the interface adhesion using various chemical treatments. Chemical exchanges between lime and fibres, in term of degradation of fibres structure with alkaline medium and effects of compounds present in fibres are modified by the chemical treatments carried out. Indeed, each treatment has a direct action on fibres surface:

- Treatment with caustic soda cleans fibres, removing the amorphous compounds, which increases index of crystallinity of fibres and thus improve the stress average and the rupture as well as the rigidity of mortars.
- EDTA treatment increases stress rupture of mortars, however this chemical treatment involves a diminution of the amount of calcium adsorbed on the fibres surface. Calcium present on the surface has an impact on the stress rupture of the composites. Perhaps this phenomenon is due to the fact that EDTA, a strong calcium complexant, destroys the pectin/calcium complex present on the surface of fibres. According to the infrared spectra, calcium pectates are always present at the surface of fibres, but with a modified structure which does not allow calcium binding.
- PEI treatment involves an intermediate behavior of all the studied properties, but its effect on mechanical properties is not prevalent.
- Lime water treatment improves only the rigidity of mortars.

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